

Computational Astrochemistry and Molecular Astrophysics

C Puzzarini, Dipartimento di Chimica "Giacomo Ciamician", Bologna, Italy

© 2014 Elsevier Inc. All rights reserved.

Introduction	1
Laboratory Studies	2
Computational Chemistry	2
Molecular Spectroscopy	3
Examples and Discussion	3
Computational Studies	3
Glycine: a potential interstellar biomolecule	3
Organic molecules in Titan's atmosphere: cyclopropenyl cation and oxirane	4
Astronomical detection of ions in the ISM	5
Rotational Spectroscopy	5
THz measurements	5
Accurate rest frequencies	6
Collisional broadening of rotational lines	6
References	6

Introduction

Astrochemistry and molecular astrophysics are interdisciplinary fields involving chemistry, physics, and astronomy. Their main aim is to understand the chemical evolution of the universe. Astrochemistry and molecular astrophysics are often used as synonym and a distinct line between them is difficult to place. Both research areas study the formation and destruction of molecules in space, their interaction with radiation and their feedback on physics of the environments. As a sort of simplification, it can be affirmed that astrochemistry focuses on the study of the chemical processes at work in space and on the understanding of the molecular evolution, trying to address the question of molecular complexity. On the other hand, molecular astrophysics is more interested in the information that can be retrieved from the study of molecules in the universe. In fact, molecules being ubiquitous (they are found everywhere in space: in interstellar, circumstellar and pregalactic gas, in protostellar disks, in the atmospheres of stars and planets, ...) are unique probes to retrieve information on molecular excitation, radiative transfer, and kinematics. In a few words, this simplification affirms that astrochemistry studies the evolution of molecules abundance, while molecular astrophysics studies the molecules as physical diagnostics. In other words, we can say that astrochemistry is the study of the abundance and reactions of chemical elements and molecules in the universe, and their interaction with radiation, while molecular astrophysics concerns the study of emission from molecules in space. The line between astrochemistry and molecular astrophysics being so fine and vague, will not be addressed further, while the two fields will be considered as parts of the same research areas.

The approach at the basis of astrochemistry and molecular astrophysics is depicted in Figure 1. Both fields span astronomical observations, modeling, and theoretical and/or experimental laboratory-based investigations. From this figure it is apparent how wide the corresponding research field is; consequently, it cannot be exhaustively addressed in this contribution. Interested readers are therefore referred to the 'Further Reading' section, whereas we limit our discussion to the role played by quantum chemistry in the field of astrochemistry as well as to the contribution of experimental rotational spectroscopy to molecular astrophysics. Quantum-chemical calculations are mainly employed in the 'laboratory' studies: spectroscopic characterizations that may support astronomical observations as well as investigations of chemical reactions (also including processes on grains) to determine thermochemistry, kinetics, and reaction mechanisms. In the latter context, actual studies are those that aim at understanding the level of complexity that can be reached by molecular species in space. Experimental laboratory studies range from the field of molecular spectroscopy (which involve observation of transitions between different energetic levels, either rotational or vibrational or electronic) to simulations of the reaction conditions in extraterrestrial environments (which involve, e.g., the study of ion-neutral reactions, of reactions taking place in either aerosols or cold plasma, etc.).

About 180 molecules have been detected in space, with at least 175 molecules observed unambiguously in the interstellar medium (ISM) or circumstellar shells and more than 50 molecules detected in extragalactic sources (see, e.g., the Cologne database^{1,2}). Our knowledge on the universe chemical inventory has been obtained and continuously updated by means of astronomical observations, which have revealed a plethora of molecular species,³ thus demonstrating the rich chemistry of the universe. Molecules can exist in a wide range of astrophysical environments, from the extremely cold regions between stars to the atmospheres of stars themselves. Gas-phase species have been mostly discovered via their rotational signatures, with the corresponding frequencies going from the millimeter-wave region up to the far-infrared, even though spectroscopies in the visible and infrared domains have also led to the detection of molecular species. The observation of gas-phase species performed using rotational spectroscopy can be undertaken from the ground,⁴ while vibrational spectroscopy observations, for which ground-based

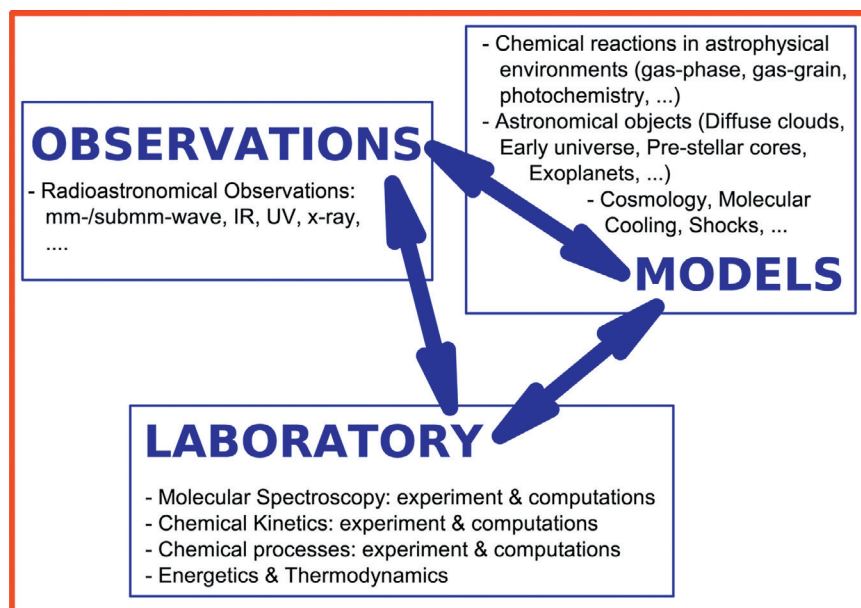


Figure 1 The approach at the basis of astrochemistry and molecular astrophysics.

observations are hampered by the terrestrial atmosphere, are mainly carried out by spectrometers on board satellites or airbornes. In particular, infrared spectroscopy is suitable for retrieving the chemical composition of planetary atmospheres. As concerns the dimension, the molecules detected ranges from diatomics to species containing more than ten atoms, up to polycyclic aromatic hydrocarbons that were identified to be abundant, for instance, in the atmosphere of Titan, Saturn's largest moon. The detection also includes isotopic species. Up to now, most of the molecules that have been detected in the ISM or elsewhere in space are neutral species. Some cations have also been found, along with only a few anions whose discovery is quite recent.

This contribution is organized as follows. In the next section, a brief overview on laboratory studies with emphasis on computational chemistry and molecular spectroscopy is provided. Thereafter, selected exemplificative cases are presented and discussed. The contribution is completed with a 'Further Reading' section.

Laboratory Studies

Computational Chemistry

As mentioned above, in the field of astrochemistry and molecular astrophysics quantum-chemical calculations can be used to provide spectroscopic characterizations that can guide the observation in the laboratory or even directly in space. To support experimental investigation, theoretical predictions should be accurate and thus imply high-level quantum-chemical calculations to be used. The focus is here on rotational and vibrational spectroscopies. The theoretical prediction of the corresponding spectra involves two tasks, namely (a) the determination of the required spectroscopic parameters, and (b) the simulation of the spectra based on the given set of spectroscopic parameters. The latter typically involves the diagonalization of an appropriate Hamiltonian, while the accurate determination of the spectroscopic parameters requires a quantum-mechanical treatment of the molecular system under consideration. To fulfill the accuracy requirements, the key point is the employment of the coupled-cluster (CC) level of theory. In particular, the CC singles and doubles (CCSD) approximation augmented by a perturbative treatment of triple excitations (CCSD(T))⁵ provides a good compromise between accuracy and computational cost. On the other hand, for large systems methods rooted in the density functional theory are demonstrated to provide results that meet the spectroscopic accuracy requirements.⁶ For exhaustive accounts on the quantum-chemical calculations of rotational parameters, the readers are referred to Refs. [7–9], while for vibrational spectroscopy Refs. [10–15] (and references therein) provide an overview of methodological and computational approaches (for both perturbative and variational models). Here, we only briefly mention that composite schemes are largely employed in order to account for various contributions (basis-set and electron-correlation effects) separately at the highest possible level and to combine them for obtaining the best possible theoretical estimates (see, e.g., Ref. [16] and references therein). Similar computational requirements are needed for accurate thermochemistry investigations: CC techniques in conjunction with composite schemes permit to obtain a sub-kJ mol^{−1} accuracy (see, e.g., Refs. [17–20]).

For an accurate modeling of the chemistry that takes place in chemistry space, the understanding of chemical kinetics in astrophysical environments is a challenge and plays an important role. In fact, it requires to predict reaction rate coefficients for temperatures (250–2000 K) and conditions well outside those commonly encountered in terrestrial laboratories. Quantum-chemical calculations can also be employed in the field of chemical kinetics, not only in the modeling of the potential energy surface (PES) (thus

pointing out reaction barriers to be overcome) but also in the determination of reaction rate constants. For the latter, stochastic or (semi-) classical approaches can be employed. On general grounds, master equations should be formulated and then solved either analytically or with numerical techniques. Refs. [21,22] provide explicative examples involving systems of interest to the present context (the HO + CO reaction and the formation of glycine, respectively).

Molecular Spectroscopy

As mentioned above, molecular species detected in space have been mostly identified via their rotational signatures, which in turn were previously measured in laboratory or obtained from the rotational parameters determined from laboratory studies. Due to its relevance in the field of molecular astrophysics and the limited account here reported, only rotational spectroscopy will be considered in this contribution from the experimental point of view.

Rotational transitions typically lie in the range of 3 GHz–3 THz,²³ with rotational constants being the parameters that mainly govern a rotational spectrum. Therefore, detections in the millimeter and submillimeter wavelength range are usually limited to the study of small- to medium-sized molecules, while measurements in the centimeter-wave region allow one to investigate larger molecules, even of biological relevance, and molecular complexes. Rotational spectroscopy can be performed either in the time or frequency domain. In the first case, the typical resolution and frequency accuracy are about 5–20 kHz and ~ 1 –5 kHz, respectively, while in the latter case the resolution is mainly limited by Doppler effect, the resolving power being 50 kHz–2 MHz, according to the frequency range considered. The Lamb-dip technique²⁴ is a powerful tool for obtaining sub-Doppler resolution in the high frequency regime, even up to the terahertz frequency range.²⁵

Examples and Discussion

As mentioned above, too vast are the fields of computational astrochemistry and molecular astrophysics to provide an exhaustive overview in this contribution and several are the possible applications of quantum-chemistry and/or molecular spectroscopy. In the following, an attempt of providing a brief but significative collection of examples is made. First, computational studies will be addressed, while in the second part of this section examples of applications of rotational spectroscopy to the field of Astrophysics will be discussed.

Computational Studies

Computational chemistry allows us to infer how complex molecules can be formed in the ISM, to understand which molecular species exist in space (planets' atmospheres, ISM, etc.), and to support or to provide the spectroscopic characterization required for astronomical observations.

Glycine: a potential interstellar biomolecule

The existence of biological building-block molecules in the ISM has attracted a great interest, especially because of their direct connection with the chemical evolution of the universe. Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) is the simplest amino acid and therefore it has been intensively searched for in the ISM. While glycine has been discovered in some meteorites fallen in Earth (e.g., Murchison meteorite²⁶) and within the returned samples of comet 81P/Wild2 from the Stardust mission,²⁷ its detection in the ISM has been debated. Despite several experimental works, direct measurements to elucidate reaction mechanisms are difficult to perform, while quantum-chemistry can be used to shed light on the mechanistic steps of the amino acids formation in the ISM by exploring the corresponding PESs.

Recent studies (see Ref. [16] and references therein) demonstrated that state-of-the-art quantum-mechanical approaches permit to accurately and fully characterize the conformational behavior of glycine, with conformational enthalpies determined well within the chemical accuracy. As is evident from Table 1 of Ref. [16], the gas-phase thermodynamic properties were obtained with a 1 kJ mol^{-1} accuracy. It is worthwhile noting that the same accuracy also applies to the transition state structures connecting the local minima on the PES. Such result is an important step toward the identification of the formation mechanism of glycine in the ISM.

Rimola et al.²² recently proposed a possible path for the formation of glycine-derivative species which may explain the discovery of glycine in some meteorites and comets. The water-dominated ice mantle covering a silicate-based core of an interstellar grain was simulated by means of a cluster of eight water molecules. The key point of the reaction mechanism is the formation of OH surface radical species due to ionizing particles, such as cosmic rays. If ice contains CO and methylenimine (NHCH_2), the reaction occurs via the formation of the COOH radical due to the coupling of the OH radical with an incoming CO molecule. Subsequently, by reacting with NHCH_2 the COOH radical yields a radical glycine-derivative species, which finally leads to glycine by the addition of one H atom. While interested readers are referred to Ref. [16] for a complete account, here we point out that quantum-chemical calculations, in addition to explain the formation of glycine on interstellar grains, can also provide information on the reaction rates. In fact, as pointed out above, the Gibbs free energy of the reaction transition state required in Eyring's equation can be accurately determined, thus allowing one to estimate the reaction rate at a given temperature with good accuracy. This is indeed a key information in order to indicate whether reactions are feasible or not on astronomical time scales.

Organic molecules in Titan's atmosphere: cyclopropenyl cation and oxirane

There is a great interest in Titan's atmosphere due to the fact that recent measurements revealed that Titan's atmosphere is characterized by a rich and complex organic chemistry (see Ref. [28] and references therein). Titan is thought to represent a model of primitive earth because its atmosphere contains significant quantities of carbon ($\sim 2\%$ CH_4) and nitrogen (98% N_2), and traces of oxygen (~ 50 ppm CO).²⁹ Photochemical production of complex molecules containing C, N, O, and H is therefore possible, and consequently, the investigation of Titan's atmosphere might provide an unique opportunity to shed light on the organic evolution in the atmosphere of early Earth.

The ion and neutral mass spectrometer (INMS) onboard the Cassini spacecraft revealed the presence of carbocations, such as CH_3^+ , CH_5^+ , C_2H_3^+ , C_2H_5^+ , C_3H_5^+ , and C_3H_7^+ , in Titan's atmosphere. In Ref. [28], based on INMS Cassini observations, on the analysis of laboratory crossed molecular-beam measurements, and on ab initio studies of the reactions of CH_3^+ with ethylene and acetylene, it was inferred that a significant fraction of the C_3H_3^+ detected by INMS in Titan's upper atmosphere is the cyclopropenyl cation, which is the simplest Huckel's aromatic molecule. Furthermore, an important class of reactions in Titan's upper atmosphere, such as those of CH_3^+ with methylacetylene and dimethylacetylene, were identified. The latter reaction explains the observed composition of C_4H_5^+ and C_5H_7^+ in terms of methyl-substituted and dimethyl-substituted cyclopropenyl cations, respectively.

Huckel's cyclic molecules are stabilized by aromaticity. Formation of aromatic compounds is an important issue because the chemistry of Titan's upper atmosphere may shed light on the first steps toward a mechanistic theory of the terrestrial prebiotic chemistry. In fact, it has been largely accepted that Titan could represent a model of primitive earth.²⁹ Investigation of Titan's atmosphere requires quantum-chemical calculations of the energetics of the reactions and molecular species involved as well as astronomical (rotational as well as infrared) observations. The latter in turn are based on either experimental or theoretical laboratory studies.

Recent photochemical models suggest that oxygen should be incorporated into the chemistry of Titan's atmosphere.³⁰ Experimental simulations of Titan's atmosphere which includes CO at the 100 ppm level on N_2 - CH_4 mixtures led to the detection of an important prebiotic species, oxirane ($\text{C}_2\text{H}_4\text{O}$, also named ethylene oxide), in the products mixture.³¹ Since INMS is not able to mass resolve the CO molecule from the major species N_2 and, on a similar basis, heavier molecules or ions, the identification of oxirane in Titan's atmosphere is demanded to astronomical observations either in the infrared region or in the millimeter/submillimeter-wave regime. The required spectroscopic characterization can be carried out either experimentally or theoretically. Focusing on rotational spectroscopy, Figure 2 demonstrates the accuracy that can be reached nowadays by high-level quantum-chemical calculations: for selected rotational transitions, experiment³² and theory³³ are compared. It is noted that the calculated transitions are on average underestimated by about 0.1%. Therefore, theoretical predictions are sufficiently accurate for either laboratory or astronomical assignments.

Moving to the field of vibrational spectroscopy, once again oxirane offers an interesting example. Bernstein and Lynch demonstrated a close correlation between the IR spectra of oxirane and cyclopropenylidene ($\text{c-C}_3\text{H}_2$) with the major unidentified

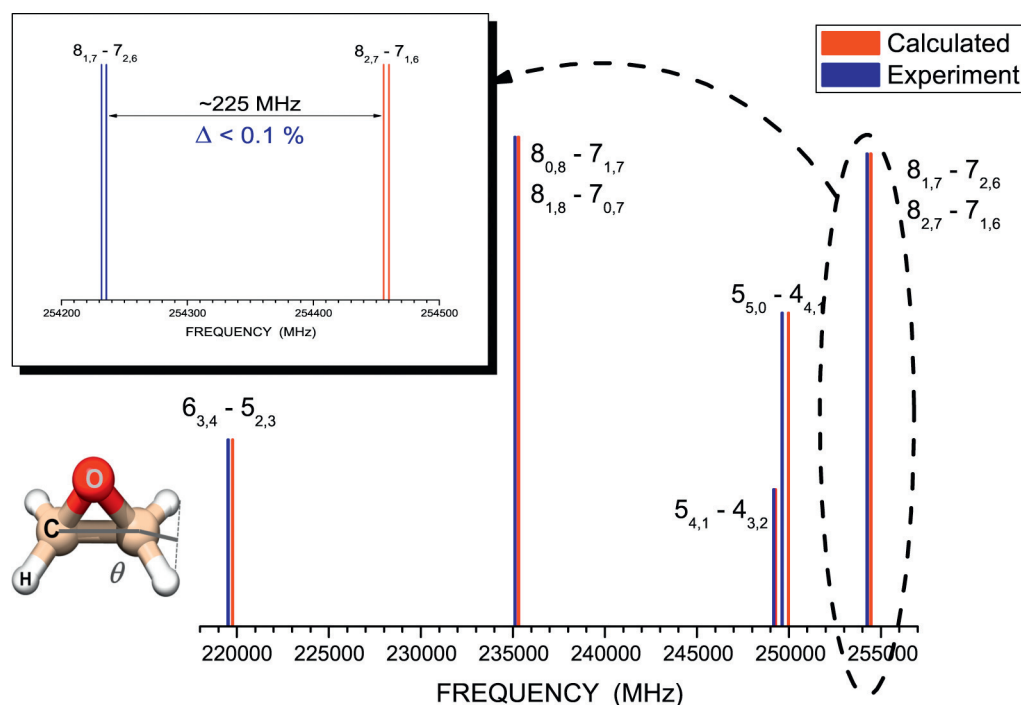


Figure 2 Comparison of calculated and experimental rotational spectrum of oxirane in the 220–260 GHz.

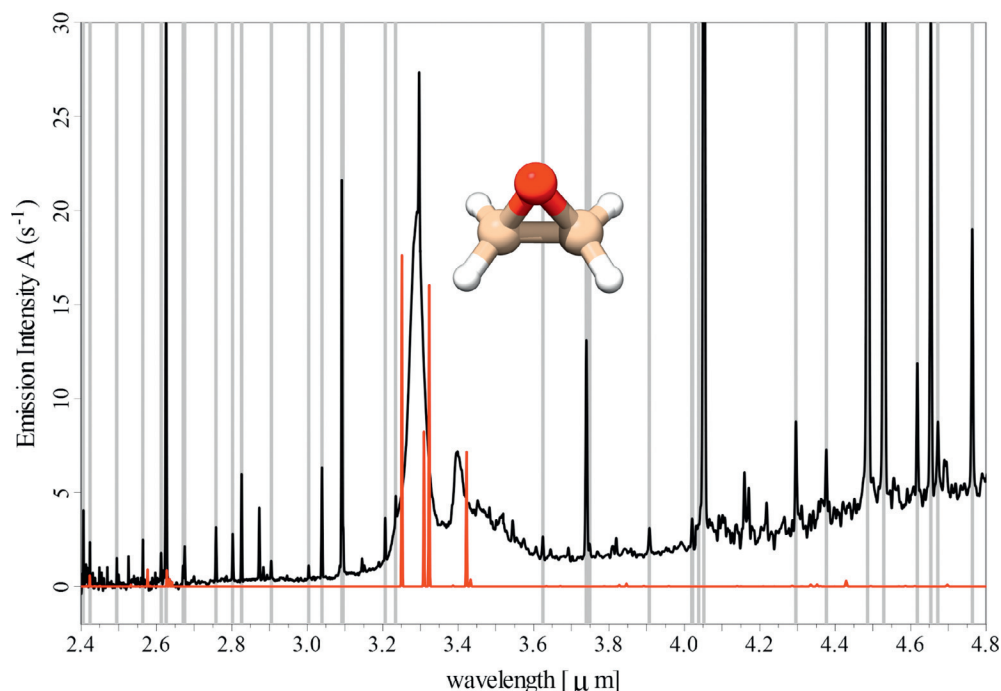


Figure 3 The comparison in the 2.4–4.8 μm wavelength range between the simulated emission spectra of oxirane (red, lower trace) and the observed spectra (black, upper trace; from the uniform database of 2.4–45.4 μm ISO-SW spectrum of planetary nebula NGC 7027³⁵) is shown. Identified line fluxes reported by Salas et al.³⁶ are marked by gray lines.

infrared (UIR) bands.³⁴ However, they also pointed out considerable uncertainties in some of the assignments and therefore called for a quantitative simulations of UIR spectra that properly account for anharmonicity effects on both line positions and intensities. **Figure 3** shows the simulation of the IR spectrum of oxirane in the 2.4–4.8 μm based on high-level quantum-chemical computations, also accounting for anharmonic effects,³³ compared with the corresponding observation (ISO-SW spectrum of the planetary nebula NGC 7027³⁵). The portion depicted also shows all identified line fluxes.³⁶ We note that the intense features of oxirane permit to explain the observed UIR features in the 3.2–3.4 μm range.

Astronomical detection of ions in the ISM

The presence of negative ions in the ISM was predicted many years ago on general grounds or on the basis of ion-molecule chemical models (see, e.g., Ref. [37]). It was pointed out that a high electron affinity and a large number of vibrational states increase greatly the sticking coefficient of electrons; for instance, large, negatively charged carbon chains of the form C_nH^- were predicted to be quite abundant. However, for a long time negative ions escaped detection because of the lack of accurate transition frequencies. Only in 2006, the first negative molecular ion C_6H^- was detected in the laboratory and identified in the molecular envelope of IRC 10216 and in the dense molecular cloud TMC-1.³⁸ The spectroscopic constants derived from laboratory measurements were found identical to those derived from the astronomical data, thus leading to the unambiguous identification of C_6H^- in the ISM.

The missing observation of anions until 2006 was due to the lack of accurate transition frequencies. Quantum-chemical calculations played a crucial role in the identification of C_6H^- in the ISM; in fact, the laboratory observation was guided by CCSD(T) computations. In 2008, a series of lines detected in the envelope of the C-rich star IRC+10216 was assigned to C_5N^- .³⁹ In this case, the assignment based on chemical and spectroscopic argumentations was confirmed by a perfect match with highly accurate computed rotational parameters.

Rotational Spectroscopy

As already mentioned, laboratory measurements of rotational transitions permitted the subsequent astronomical detection of most of the molecules discovered in space. In the following, a few exemplificative cases have been selected in order to present further or innovative applications of rotational spectroscopy in the field of molecular astrophysics.

THz measurements

Herschel Space Observatory, Stratospheric Observatory for Infrared Astronomy (SOFIA), and Atacama Large Millimeter Array (ALMA) opened up the submillimeter-wave region of the electromagnetic spectrum by making astronomical investigations of unprecedented high sensitivity and angular resolution possible. If on one hand the great spectral resolution that can be exploited by ALMA is expected to play a key role in the detection of complex species as well as rare isotopologues, on the other hand already the

first spectra recorded by Herschel turned out to be full of signatures, mostly unassigned. Unfortunately, a few molecular species show extremely numerous and relatively strong transitions throughout the submillimeter-wave region. Consequently, these species are likely to be a serious challenge as their emission occupies a substantial part of the spectral ranges available, thus impeding the study of other important species. The discovery of new species of astrophysical and astrobiological interest is therefore severely hampered unless the spectral lines from these ‘weeds’ can be removed from the data. For these reasons, accurate laboratory measurements in the submillimeter-wave and THz frequency ranges are required, and a great effort has been made in this direction.

Transition frequencies in the region of the electromagnetic spectrum mentioned above require to be known with an accuracy preferably better than 100 kHz, thus leading to the need of extending laboratory data. Furthermore, extrapolations from low-frequency laboratory measurements might provide inaccurate and/or not reliable higher frequencies. An exemplificative case is provided by the experimental determination of the sextic centrifugal-distortion constant of HCO^+ (formyl ion), the most abundant molecular ion in the ISM, observed and observable in many objects. The results summarized in Table 2 of Ref. [40] point out the importance of accurate measurements in the submillimeter-wave region up to the THz in order to correctly determine the sextic centrifugal-distortion constant. In a previous work the attempt of evaluating it even provided a value with the wrong sign. The importance of a correct determination of these small spectroscopic terms is due to the fact that they play a key role in the prediction of rotational transitions at higher frequency, which in turn can be used for the identification in space of the molecular species under consideration. In passing, we note that the determination of unreliable spectroscopic parameters can be avoided if accurate computational data are used to support the fitting procedure.

Accurate rest frequencies

Although the available accuracy for most interstellar lines (~ 100 kHz) is sufficient for confident identification, detailed studies of molecular excitation, radiative transfer, systematic velocity gradients, and ambipolar diffusion in star-forming regions need significantly higher accuracy. Furthermore, the accuracy of astronomical observations is strongly influenced by the uncertainties of the various Doppler corrections due to the Earth motion. The best way to avoid such errors is to measure simultaneously the studied lines and the line of some other molecule with precisely known rest frequency (frequency standard). In Ref. [41], it was shown that rotational spectroscopy by means of Lamb-dip technique can fulfill the accuracy requirements for establishing frequency standard, because it permits to retrieve transition frequencies with an accuracy of about 1 kHz. In detail, in Ref. [41] the Lamb-dip technique allowed us to perform the most precise laboratory measurements of the rotational transitions of C^{18}O , thus leading to very accurate spectroscopic constants that permit to consider C^{18}O as a frequency standard for radio astronomical spectroscopy. While the main CO isotopologue cannot be used as a frequency standard because its rotational lines have extremely high opacity, C^{18}O was selected because its lines are usually optically thin.

The discussions reported above and in the previous section point out the need of accurate measurements of rotational transitions, with particular emphasis on the THz region. While sub-Doppler resolution and the accuracy that this implies are well consolidated in the millimeter/submillimeter-wave region, completely different is the situation in the THz frequency range. Despite the explosive growth undergone by the corresponding technology in the last decade, the achievement of sub-Doppler resolution in this frequency region is only at its beginning (see Ref. [25] and references therein). In Refs. [25,42], it has been demonstrated that an accuracy of 1 kHz (i.e., an accuracy better than one part in 10^9) can be obtained in the THz region and how this accuracy permits to improve the spectroscopic parameters determination.

Collisional broadening of rotational lines

Collisional and radiative excitations are two important mechanisms which determine the existence and shape of spectral lines in the ISM. Therefore, collisional rates and transition moments are needed in order to interpret interstellar spectra in terms of local physical conditions. Experimental estimates for collisional rates rely on measurements of collision-induced spectral pressure broadening.⁴³ A significant example is provided by the investigation on N_2H^+ perturbed by He, reported in Ref. [44]. N_2H^+ , one of the first molecular ions detected in interstellar space, plays an important role in understanding the physical conditions in protostellar cores, and has thus been the subject of extensive studies. From a computational point of view, the accurate knowledge of the PES for the N_2H^+ -He interaction allows calculations of state-to-state collisional transitions rates, which are then used for probing the observations from interstellar molecular clouds. While a direct check of the accuracy of these calculations is not possible, the scattering matrix used can be validated by means of pressure-broadening and pressure-shift measurements.⁴⁴ These are measurements in which the collisional width and frequency are determined at different pressure values of the perturber (He in the example considered) and the corresponding pressure-broadening and pressure-shift coefficients derived.

References

1. Müller, H. S. P.; Thorwirth, S.; Roth, D. A.; Winnewisser, G. *Astron. Astrophys.* **2001**, 370, L49–L52.
2. Müller, H. S. P.; Schöder, F.; Stutzki, J.; Winnewisser, G. *J. Mol. Struct.* **2005**, 742, 215–227.
3. Tielens, A. G. G. M. *Rev. Mod. Phys.* **2012**, 85, 1021–1081.
4. Herbst, E.; van Dishoeck, E. F. *Annu. Rev. Astron. Astr.* **2009**, 47, 427–480.
5. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, 157, 479–483.
6. Barone, V.; Baiardi, A.; Biczysko, M.; Bloino, J.; Cappelli, C.; Lipparini, F. *Phys. Chem. Chem. Phys.* **2012**, 14, 12404–12422.
7. Puzzarini, C.; Heckert, M.; Gauss, J. J. *Chem. Phys.* **2008**, 128, 194108.

8. Puzzarini, C. *Phys. Chem. Chem. Phys.* **2013**, *15*, 6595–6607.
9. Puzzarini, C.; Stanton, J. F.; Gauss, J. *Int. Rev. Phys. Chem.* **2010**, *29*, 273–367.
10. Barone, V. *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*; Elsevier, 2013. <http://dx.doi.org/10.1016/B978-0-12-409547-2.05400-7>.
11. Barone, V.; Biczysko, M.; Bloino, J. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1759–1787.
12. Puzzarini, C.; Biczysko, M.; Barone, V. *J. Chem. Theory Comput.* **2010**, *6*, 828–838.
13. Bowman, J. M. *Science* **2000**, *290*, 724–725.
14. Vázquez, J.; Stanton, J. F. *Mol. Phys.* **2007**, *105*, 101–109.
15. Christiansen, O. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2942–2953.
16. Barone, V.; Biczysko, M.; Bloino, J.; Puzzarini, C. *Phys. Chem. Chem. Phys.* **2013**, *15*, 10094–10111.
17. Tajti, A.; Szalay, P. G.; Császár, A. G.; Kallay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599–11613.
18. Császár, A. G.; Allen, W. D.; III, H. S. *J. Chem. Phys.* **1998**, *108*, 9751.
19. Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.
20. Peterson, K. A.; Feller, D.; Dixon, D. A. *Theor. Chem. Acc.* **2012**, *131*, 1079.
21. Weston, R. E., Jr.; Nguyen, T. L.; Stanton, J. F.; Barker, J. R. *J. Phys. Chem. A* **2013**, *117*, 821–835.
22. Rimola, A.; Sodupe, M.; Ugliengo, P. *Astrophys. J.* **2012**, *754*, 24/1–24/10.
23. Gordy, W.; Cook, R. L. In *Microwave Molecular Spectra*; Weissberger, A., Ed.; 3rd ed.; Wiley: New York, 1984.
24. Costain, C. C. *Can. J. Phys.* **1969**, *47*, 2431.
25. Cazzoli, G.; Puzzarini, C. *J. Phys. Chem. A* **2013**, *117*, 13759–13766.
26. Kenvolden, K. A.; Lawless, J.; Pering, K.; Peterson, E.; Flores, J.; Ponnampuram, C.; Kaplan, I. R.; Moore, C. *Nature* **1970**, *228*, 923–926.
27. Glavin, D. P.; Dworkin, J. P.; Sanford, S. A. *Meteorit. Planet. Sci.* **2008**, *43*, 399–413.
28. Ali, A.; Sittler, E. C., Jr.; Chornay, D.; Rowe, B. R.; Puzzarini, C. *Planet. Space Sci.* **2013**, *87*, 96–105.
29. Raulin, F.; McKay, C.; Lunine, J.; Owen, T. In *Titan from Cassini-Huygens*; Brown, E. H.; Lebreton, J.-P.; Waite, J. H., Eds.; Springer: Heidelberg, 2009; pp 215–234.
30. Hörst, S. M.; Vuitton, V.; Yelle, E. V. *J. Geophys. Res.* **2008**, *113* E10006/1–14.
31. Bernard, J.-M.; Coll, P.; Coustenis, A.; Eaulin, F. *Planet. Space Sci.* **2003**, *51*, 10031011.
32. Pan, J.; Albert, S.; Sastry, K. V. L. N.; Herbst, E.; Lucia, F. C. D. *Astrophys. J.* **1998**, *499*, 517–519.
33. Puzzarini, C.; Biczysko, M.; Bloino, J.; Barone, V. *Astrophys. J.* **2014**, *785*, 107.
34. Bernstein, L. S.; Lynch, D. K. *Astrophys. J.* **2009**, *704*, 226–239.
35. Sloan, G. C.; Kraemer, K. E.; Price, S. D.; Shipman, R. F. *Astrophys. J. Suppl. S.* **2003**, *147*, 379–401.
36. Salas, J. B.; Pottasch, S. E.; Beintema, D. A.; Wesselius, P. E. *Astron. Astrophys.* **2001**, *367*, 949–958.
37. Herbst, E. *Nature* **1981**, *289*, 656–657.
38. McCarthy, M. C.; Gottlieb, C. A.; Gupta, H.; Thaddeus, P. *Astrophys. J.* **2006**, *652*, L141–L144.
39. Cernicharo, J.; Guélin, M.; Agúndez, M.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J.* **2008**, *688*, L83–L86.
40. Cazzoli, G.; Cludi, L.; Buffa, G.; Puzzarini, C. *Astrophys. J. Suppl. S.* **2012**, *203*, 11/1–11/9.
41. Cazzoli, G.; Puzzarini, C.; Lapinov, A. V. *Astrophys. J.* **2003**, *592*, L95–L98.
42. Cazzoli, G.; Puzzarini, C. *J. Mol. Spectrosc.* **2014**, *298*, 31. <http://dx.doi.org/10.1016/j.jms.2014.02.002>.
43. Anderson, T. G.; Gudeman, C. S.; Dixon, T. A.; Woods, R. J. *Chem. Phys.* **1980**, *72*, 1332–1336.
44. Buffa, G.; Tarrini, O.; Dore, L.; Meuwly, M. *ChemPhysChem* **2010**, *11*, 3141–3145.

Further Reading

1. The interest of the chemistry community in the field of Astrochemistry is proved by the recent Chemical Reviews and Physical Chemistry Chemical Physics special issues: *Chem. Rev.* **2013**, *113* (12) Astrochemistry; *Phys. Chem. Chem. Phys.* **2014**, *16* Themed collection “Astrochemistry”.
2. Hartquist, T. W.; Williams, D. A., Eds.; *The Molecular Astrophysics of Stars and Galaxies*; Clarendon Press: Oxford, 1998; International Series in Astronomy and Astrophysics 4.
3. van Dishoeck, E. F., Ed.; *Molecules in Astrophysics: Probes and Processes*; Kluwer: Dordrecht, 1997.
4. Minh, Young C.; van Dishoeck, Ewine F., Eds.; *Astrochemistry: From Molecular Clouds to Planetary Systems*; Astronomical Society of the Pacific: San Francisco, CA, 2000.
5. Bohme, D. K.; Herbst, E.; Kaifu, N.; Saito, S., Eds.; *Chemistry and Spectroscopy of Interstellar Molecules*; University of Tokyo Press: Tokyo, 1990.
6. Lis, D. C.; Blake, G. A.; Herbst, E., Eds.; *Astrochemistry: Recent Successes and Current Challenges*; Cambridge University Press: Cambridge, UK, 2006.
7. Tielens, A. G. G. M. *The Physics and Chemistry of the Interstellar Medium*; Cambridge University Press: Cambridge, 2005.
8. Winnewisser, G.; Herbst, E.; Ungerechts, H. In *Spectroscopy of the Earth's Atmosphere and Interstellar Medium*; Eao, K. N.; Weber, A., Eds.; Academic Press, 1992.
9. Tennyson, J. *Astronomical Spectroscopy*; Imperial College Press: London, 2005.
10. Herbst, E. *Chem. Soc. Rev.* **2001**, *30*, 168.